

DESCRIPTION

HEAT RESISTANT MAGNESIUM DIE CASTING ALLOYS

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TECHNICAL FIELD

The present invention relates to a heat resistant magnesium die casting alloy and a die cast product of that alloy.

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BACKGROUND ART

In recent years, to deal with the demand for reduction of the weight of vehicles, greater application of alloys of magnesium, the lightest of the practical metals, has been desired. However, conventional die casting magnesium alloys greatly deform at high temperatures. Not much progress has been made for parts having bolted portions exposed to high temperature environments (120°C or more). Up until now, various heat resistant magnesium die casting alloys have been developed, but it has not been possible to simultaneously improve the heat resistance (high temperature strength and creep resistance) and castability (hot-cracking resistance and die-sticking resistance during die casting) and therefore the range of application has been limited.

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Therefore, to achieve both heat resistance and castability, JP-A-2001-316752 has proposed a die casting magnesium alloy comprised of 2 to 6 wt% Al, 0.3 to 2 wt% Ca, 0.01 to 1 wt% Sr, 0.1 to 1 wt% Mn, and the balance of Mg and unavoidable impurities. Due to this, it becomes possible to simultaneously improve the heat resistance and castability and expand the range of application.

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Even with the magnesium alloy of the above proposal, however, it has not been possible to sufficiently cover the range of applications required, so development of a heat resistant magnesium die casting alloy with further improved combination of heat resistance and castability

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has been desired.

DISCLOSURE OF INVENTION

The present invention has as its object to provide a heat resistant magnesium die casting alloy simultaneously improved in heat resistance and castability and expanded in range of applications and a die cast product of the same alloy.

To achieve the above object, according to the present invention, there is provided a heat resistant magnesium die casting alloy comprising, by wt%, the following composition:

Al: over 6% to not more than 10%,
Ca: 1.8 to 5%,
Sr: 0.05 to 1.0%,
Mn: 0.1 to 0.6%, and
Bal: Mg and unavoidable impurities,
the ratio Ca/Al of the Ca content to the Al content being 0.3 to 0.5.

The present invention is characterized by limiting the ratio Ca/Al of the contents of Al and Ca to within a predetermined range so as to improve the combination of the heat resistance and castability over the conventional limits without causing deterioration of characteristics even if adding Al and Ca to high contents considered unsuitable in the past.

For example, JP-A-2001-316752 sets the upper limit of the Al content to 6 wt% and the upper limit of the Ca content to 2 wt%. The reason for the limitations is explained as being that if the Al content is over 6 wt%, the creep resistance rapidly deteriorates, while if the Ca content exceeds 2 wt%, casting cracks easily occur (see paragraph 0010 to 0012 of the publication).

As opposed to this, the inventors newly discovered that by limiting the ratio Ca/Al of the Ca content to the Al content to the range of 0.3 to 0.5, even if adding Al and Ca exceeding the upper limits of the above publication, it is possible to simultaneously achieve an

improvement of the high temperature strength and castability, which are the main effects of high Al, and an improvement of the creep resistance, which is the main effect of high Ca, without causing either a drop in the creep resistance due to the higher Al or casting cracks due to the higher Ca. The present invention was completed based on this novel discovery.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a graph comparing the retained bolt loads of various types of Mg alloys.

FIG. 2 is a graph of the relationship between the high temperature retained bolt load and Ca/Al ratio.

FIG. 3 is a graph of the relationship between the casting crack length and Ca/Al ratio.

FIGS. 4A and 4B are graphs of the (A) change in corrosion weight loss and (B) change in corrosion rate with respect to the test duration of a salt water spray test for Mg alloys with various RE contents.

FIG. 5 is a graph of the change in the corrosion rate with respect to the RE content for specific test durations (numbers of days).

FIGS. 6A and 6B are graphs of the (A) 0.2% proof stress and tensile strength and the (B) elongation in the temperature range of room temperature to 250°C.

FIG. 7 is a graph comparing the high temperature retained bolt loads of a 0.44% RE material and no-addition material among the alloys of the present invention and comparing them with the conventional use alloy AZ91D.

BEST MODE FOR CARRYING OUT THE INVENTION

The composition of the heat resistant magnesium die casting alloy of the present invention is limited due to the following reasons. Note that in this description, unless otherwise specified, the "%" in the indications of the content of the components mean "wt%".

[Al: over 6% to not more than 10%]

Al raises the strength at room temperature and high

temperature by dispersion strengthening (in particular grain boundary strengthening) by forming Al-Ca-based, Al-Sr-based, and Mg-Al-based intermetallic compounds.

Further, it lowers the melting point (liquidus line) of the alloy to raise the fluidity of the melt and improve the castability. In the present invention, by including Al over 6% under a predetermined range of Ca/Al ratio, it is possible to increase the room temperature and high temperature strength over the conventional limit and secure a good castability. However, even if limiting the Ca/Al ratio to within the predetermined range of the present invention, if Al is present in excess, the creep resistance (high temperature retained bolt load) drops, so the upper limit of the Al content is made 10%.

[Ca: 1.8 to 5%]

Ca improves the proof strength at room temperature and high temperature by grain boundary strengthening by Al-Ca-based intermetallic compounds and simultaneously particularly raises the creep resistance (high temperature retained bolt load). In the present invention, by making the Ca content 1.8% to 5% under a predetermined range of the Ca/Al ratio, it is possible to improve the proof strength and creep resistance over the conventional limits in the copresence with Al. However, even if limiting the Ca/Al ratio to a predetermined range of the present invention, if Ca is present in excess, hot-cracking and die-sticking easily occur during die casting, so the upper limit of the Ca content is made 5%. The Ca content is preferably over 2% and not more than 5%, more preferably 2.5 to 3.5%.

[Ratio Ca/Al of Ca content to Al content: 0.3 to 0.5]

In the present invention, by limiting the Ca/Al ratio to this range, it becomes possible to increase the Al content and Ca content over the conventional limits without causing a drop in the creep resistance due to the higher Al or a deterioration of the castability due to

the higher Ca and therefore possible to further raise the high temperature strength and creep resistance over the past and secure a good castability. To stably secure a high creep resistance, it is necessary to make the Ca/Al ratio at least 0.3. To stably suppress the occurrence of hot-cracking during die casting, it is necessary to make the Ca/Al ratio not more than 0.5.

[Sr: 0.05 to 1.0%]

Sr is added to further improve the effect of prevention of casting cracks and securing creep resistance. To obtain this effect, it is necessary to add Sr to at least 0.05%. The effect becomes greater with increasing the amount of addition. However, even if added over 1.0%, the effect does not increase not much at all.

[Mn: 0.1 to 0.6%]

Mn is added to secure a good corrosion resistance. To obtain this effect, it is necessary to make the Mn content at least 0.1%. However, if Mn is present in excess, free Mn precipitates and embrittlement occurs, so the upper limit of the Mn content is made 0.6%.

The magnesium alloy of the present invention is remarkably improved in corrosion resistance by further adding a rare earth metal (RE) to the above composition in the range of 0.1 to 3%. To realize this effect, it is necessary to make the RE content at least 0.1%. However, if the RE content exceeds 3%, the castability rapidly deteriorates, casting cracks and misruns end up occurring, and a sound casting is not obtained, so the upper limit of the RE content is made 3%.

The heat resistant magnesium alloy of the present invention is particularly limited to one for die casting. By die casting, a fine network comprised of Al-Ca-based or Al-Sr-based intermetallic compounds is formed and a good heat resistance can be secured.

The basic process for obtaining a product by applying the alloy of the present invention to die casting is as follows:

Alloy metal → charging into crucible (*1) →
melting → temperature adjustment → die casting (*2) →
removal of product

*1) The crucible used is made of iron.

5 *2) The die casting is by a cold chamber, hot
chamber, etc.

The die casting heat resistance magnesium alloy of
the present invention is particularly advantageous when
applied to parts requiring heat resistance such as parts
10 of automobile engines, in particular, oil pans, headlight
covers, etc. and also transmission cases.

EXAMPLES

[Example 1] The following experiment was performed
to confirm the effect of improvement of the castability
15 and heat resistance by alloy compositions of the present
invention.

Mg alloys of the compositions of Table 1 were die
cast under the following conditions using a 135 ton cold
chamber die casting machine.

20 <Die casting conditions>

Shape and dimensions of die: 70w x 150L (3, 2, and
1t from gate side)... flat plate

15φ x 120L ... rod

Die preheating: 200°C

25 Casting temperature: 700 to 720°C

Casting atmosphere: 1% SF₆+CO₂

The obtained alloy samples were subjected to tensile
tests (test temperature: room temperature (RT), 150°C)
and measured for crack length at casting and bolt load
retention. As the bolt load retention, the retained bolt
30 load was measured under the following conditions. The
measurement results are shown all together in Table 2 and
Table 3.

35 <Measurement conditions of high temperature retained
bolt load>

Initial bolt load: 8 kN

Holding temperature: 150°C

Holding time: 300 h

Retained rate: bolt load before and after holding at
a high temperature measured at room temperature and
5 calculated as retained bolt load

Further, FIG. 1 is a graph showing the high
temperature retained bolt loads of different alloy
samples, FIG. 2 the relationship between the high
temperature retained bolt load and Ca/Al ratio, and FIG.
10 3 the relationship between the casting crack length and
Ca/Al ratio.

In particular, from the results of FIG. 2, it is
clear that the retained bolt load increases with
increasing the Ca/Al ratio and that to secure the
15 practically required retained bolt load of at least 70%,
it is necessary that $\text{Ca/Al ratio} \geq 0.3$.

From the results of FIG. 3, it is clear that the
casting crack length increases along with an increase in
the Ca/Al ratio and that to secure the actually required
20 crack length of not more than 600 mm, it is necessary
that $\text{Ca/Al ratio} \leq 0.5$.

From the above results, it is clear that only when
the contents of the components are in the range of the
present invention and the Ca/Al ratio is in the range of
25 the present invention can the strength (room temperature
and high temperature) and creep resistance (high
temperature retained bolt load) be improved while stably
suppressing casting cracking.

Table 1

No.	Name	Analysis values (wt%)				Ca/Al
		Al	Ca	Sr	Mn	
1	M310101	3.03	1.01	0.11	0.11	0.33
2	M310203	2.95	0.96	0.22	0.31	0.33
3	M310506	3.16	1.02	0.51	0.62	0.32
4	M320103	3.10	2.04	0.13	0.30	0.66
5	M320206	3.24	2.06	0.23	0.64	0.64
6	M320501	3.09	1.99	0.50	0.11	0.64
7	M330106	3.30	2.87	0.12	0.64	0.87
8	M330201	3.10	3.09	0.22	0.12	1.00
9	M330503	3.18	3.13	0.54	0.31	0.98
10	M510206	5.19	1.04	0.11	0.31	0.20
11	M510501	5.31	1.04	0.25	0.64	0.20
12	M510501	5.13	1.02	0.52	0.11	0.20
13	M520106	5.34	2.06	0.11	0.62	0.39
14	M520201	4.99	2.05	0.22	0.10	0.41
15	M520503	5.12	2.09	0.54	0.33	0.41
16	M530101	5.26	3.22	0.12	0.13	0.61
17	M530203	5.00	3.03	0.22	0.32	0.61
18	M530506	5.32	3.11	0.54	0.63	0.58
19	M710106	7.28	1.06	0.12	0.58	0.15
20	M710201	7.16	1.10	0.23	0.13	0.15
21	M710503	7.08	1.09	0.51	0.33	0.15
22	M720101	7.22	1.98	0.12	0.12	0.27
23	M720203	6.99	2.06	0.23	0.29	0.29
24	M720506	7.33	2.10	0.54	0.57	0.29
25	M730103	6.98	3.08	0.12	0.29	0.44
26	M730206	7.32	3.08	0.22	0.58	0.42
27	M730501	7.19	3.13	0.52	0.11	0.44

Table 2

No.	Proof strength (MPa)		Tensile strength (MPa)	
	RT	150	RT	150
1	133	118	195	144
2	119	115	196	145
3	143	127	198	169
4	165	134	186	170
5	164	137	204	176
6	166	133	187	161
7	166	148	203	179
8	183	145	217	177
9	193	154	200	170
10	199	129	209	162
11	146	133	234	173
12	148	127	220	169
13	155	142	227	182
14	156	135	188	172
15	165	143	207	175
16	177	149	206	195
17	172	146	218	186
18	181	154	215	198
19	160	132	244	178
20	158	133	232	179
21	160	136	234	178
22	174	145	230	189
23	166	146	229	182
24	174	148	217	190
25	176	152	234	197
26	173	156	236	203
27	177	155	231	204

Table 3

No.	Crack length (mm)	Retained rate after 300 h (%)
1	2770	55.90
2	3500	61.90
3	2310	63.43
4	2614	70.36
5	1174	70.26
6	1694	79.79
7	792	74.79
8	1852	81.62
9	3098	77.59
10	514	52.73
11	386	48.39
12	544	62.13
13	512	67.71
14	558	78.26
15	346	81.70
16	744	80.69
17	1020	77.39
18	842	80.16
19	0	15.70
20	10	21.43
21	8	30.42
22	300	62.34
23	548	61.38
24	314	68.00
25	456	79.83
26	134	81.61
27	230	88.89

[Example 2] The following experiment was performed to confirm the effect of improvement of the corrosion resistance by RE addition in the alloy composition of the present invention.

The Mg alloys of the compositions of Table 4 were die cast in the same way as in Example 1. The alloy compositions of No. 101 to 105 shown in Table 4 were basically comprised (target values) of 7%Al-3%Ca-0.5%Sr-0.3%Mn with amounts of RE added (target values) of successively 0% (no addition), 0.1%, 0.5%, 2.0%, and 3.0% (analysis values of added RE elements of 0.08%, 0.44%, 1.77%, and 2.68%). For the RE addition, a Ce-rich (50%) misch metal was used.

The obtained alloy samples were subjected to salt

water spray tests under the following conditions to evaluate the corrosion resistance.

<Salt Spray Test Method>

- 5 1. Cut out test piece (width 70 mm x length 50 mm
x thickness 3 mm) from the die cast product in the as-
cast state.
2. Immerse the test piece in acetone and
ultrasonically clean it for 15 minutes, then measure its
weight (initial weight).
- 10 3. Mask the parts of the surface of the test piece
finished being measured for weight other than the as-cast
surface (test surface).
4. Perform the salt spray test by a 5% NaCl
aqueous solution under conditions defined in JIS Z2371.
- 15 5. After the end of the test, boil and clean the
test piece by a 15% chromic acid aqueous solution for 1
minute so as to remove the corrosion product on the
surface of the test piece.
6. Dry, then measure the weight of the test piece
20 and use the difference from the initial weight as the
corrosion weight loss. Further, divide the value of the
corrosion weight loss by the test area and the number of
test days and use the result as the corrosion rate.
- FIG. 4A and FIG. 4B show changes in the corrosion
25 weight loss and corrosion rate for different test
durations (numbers of days). Compared with the no-RE
material 101, the RE-added materials 102 to 105 all had
small corrosion weight losses and small corrosion rates.
At FIG. 4A showing the change along with time of the
30 corrosion weight loss, the curves are convex upward. In
FIG. 4B converting this to the change along with time of
the corrosion rate, the curves are convex downward. Along
with the elapse of the test duration, there is a tendency
for the corrosion to proceed slower.
- 35 FIG. 5 is a graph of the effects of the RE content
on the progression of corrosion. The corrosion rate was
plotted against the RE content for a test duration of one

day and 10 days. At both test durations, the corrosion rate clearly decreases by the addition of 0.08% of RE as compared with no RE (0%). With increasing the amount of addition of 0.44% and 1.77%, the corrosion rate further decreases. However, if increasing the amount of addition to 2.68%, the corrosion rate conversely starts to increase, but even so the corrosion rate is far smaller than with no addition. By adding RE in a range of 0.1% to 3% according to the present invention, it is learned that the corrosion resistance is remarkably improved compared with no addition.

Next, the effects of the addition of RE on the strength properties and creep resistance properties were investigated.

As a typical composition of the RE-added material, a 0.44%-added material (103) was compared with the non-addition material (101). FIGS. 6A and 6B show the (A) 0.2% proof strength and tensile strength and (B) elongation at the test temperature from room temperature to 250°C. At all test temperatures, it was learned that the 0.44% RE material (◆ plot) was provided with similar strength characteristics to the non-addition material (○ plot).

FIG. 7 compares the high temperature retained bolt loads of a 0.44% RE material (103), a non-addition material (101), and an AZ91D (typical known heat resistant Mg die casting alloy). The test procedure was the same as that in Example 1.

First, it is learned that the alloy of the present invention is far larger in retained bolt load compared with the conventional use alloy AZ91D regardless of the addition of RE.

Further, in the alloys of the present invention, the 0.44% RE material (103) fell in retained bolt load by about 10% compared with the non-addition material (101), but sufficiently secured the practically required at least 70%, so was provided with both the practically

sufficient heat resistance and corrosion resistance. Simultaneously, an excellent castability was also provided and it was possible to die cast without any problem.

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Table 4

No.	Name	Analysis values (wt%)								Ca/Al
		Basic alloy components				Rare earth metal				
		Al	Ca	Sr	Mn	Total	Ce	La	Nd	
101	M730503	7.08	2.86	0.50	0.31	0	0	0	0	0.40
102	M73050301	6.75	3.24	0.54	0.16	0.08	0.04	0.03	0.01	0.48
103	M73050305	6.83	2.85	0.50	0.26	0.44	0.22	0.13	0.09	0.42
104	M73050320	6.85	2.89	0.48	0.25	1.77	0.91	0.55	0.31	0.42
105	M73050330	7.13	2.93	0.50	0.34	2.68	1.33	0.78	0.57	0.41

INDUSTRIAL APPLICABILITY

According to the present invention, a heat resistant magnesium die casting alloy simultaneously improved in heat resistance and castability and able to be used for a wider range of applications than the past is provided.

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Further, due to the RE addition, in addition to the heat resistance and castability, the corrosion resistance may also be simultaneously improved.